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Vapor-Phase Lubricants: Nanometer-Scale Mechanisms and Applications to Sub-micron Machinery.

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13. ABSTRACT ***(Maximum 200 Words)***

TCP (tricresylphosphate) is a high-temperature vapor-phase lubricant, known for its demonstrated anti-wear properties for macroscopic systems and potential for MEMS applications. We have performed adsorption measurements of TCP on high purity iron and chromium surfaces with a quartz crystal microbalance , in conjunction with Auger electron spectroscopy and scanning tunneling microscopy, yielding values for gas uptake rates, molecular slippage, and tribofilm stress levels in the temperature range 25 - 400 C. At room temperature, TCP uptake is observed to be limited to two layers of intact molecules that are likely to be physisorbed. Above 200C, the data recorded on both iron and chromium substrates are consistent with far greater uptake levels and extensive interdiffusion of TCP fragments with the substrate. The most noteworthy difference between the two substrates is TCP's fragmentation upon impact on iron, but not chromium, at elevated temperatures.

The effect of oxygen on film formation has also been studied Above 300°C, sizeable frequency and amplitude shifts are observed for oxygen and TCP on iron, interpreted as the formation of a viscoelastic 'polymer-solid matrix' on the iron surface. The absence of such shifts for chromium indicates its lack of reactivity. These findings corroborate TCP's known ability to lubricate iron, but not chrome. **We have thus successfully mapped atomic scale dynamical properties to the lubricant's macroscopic performance..**

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Final Technical Report

Vapor Phase Lubricants: Nanometer-scale Mechanisms and Applications to Sub-micron Machinery, **Award # F49620-01-1-0132**
Funding Period: 01/01/01 – 12/31/03

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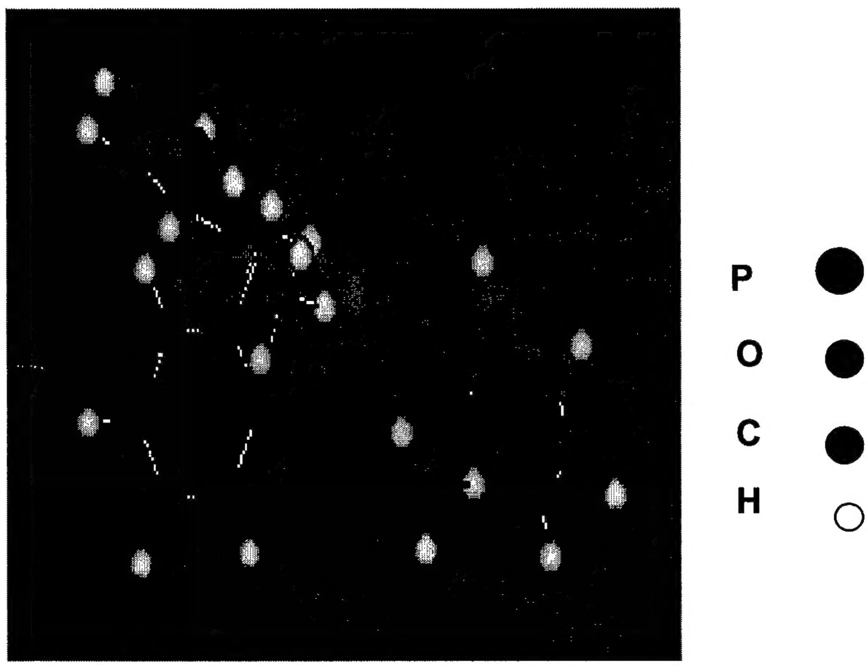


3D-TRICRESYL PHOSPHATE

Research Objective:

The objective of the research funded by **AFOSR#F49620-01-1-0132** was to quantify at nanometer length-scales the fundamental mechanisms which are believed to underlie the lubricating properties of TCP and TBPP on metallic substrates such as iron, chrome and copper. Auger Spectroscopy, Quartz Crystal Microbalance (QCM) and Scanning Tunneling Microscopy (STM) measurements are performed to document mass uptake, diffusion and dynamical properties at temperatures up to 500C. Nanotribological properties are also probed at realistic sliding speeds by means of a STM tip sliding along the surface electrode of a QCM electrode.

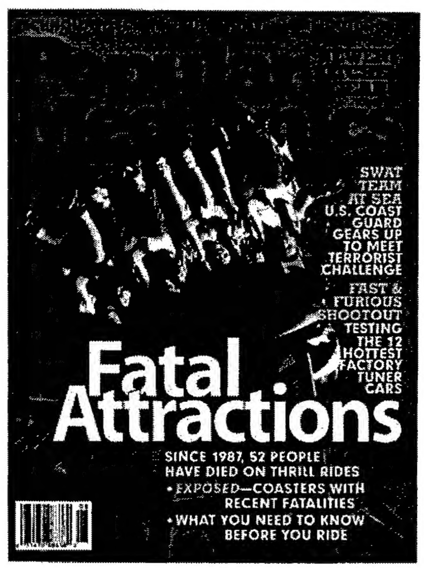
The technical payoff to DOD of this research is:

•Improved lubricant performance in extreme environments where conventional liquid lubricants are nonviable. (Turbine engines, Low Heat Rejection Engines, MEMS devices, Low temperature and/or Space Environments, etc.)

•Prediction of lubricant performance in advance of development of new materials.

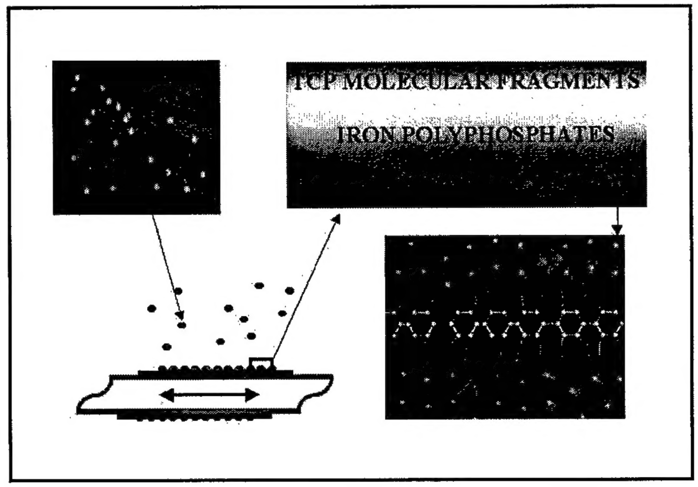
(1) (2) Summary of Research Activities and Accomplishments
We have performed adsorption measurements of tricresylphosphate (TCP) on high-purity iron, chrome and oxide film surfaces, yielding values for gas uptake rates in the temperature range 25 - 400 C. and extended the measurements to include studies of the role of oxygen, and to include extensive dynamical characterizations of the adsorbed species. In doing so, we have successfully documented the conditions under which lubricious polymeric friction film formation occurs.

In order to study the lubricants' performance at realistic sliding speeds, we constructed an STM-QCM apparatus for imaging and friction experiments whereby the topography of the substrate is compared before, during and after tip-surface contact or tunneling contact though the lubricant layer. In addition, we collaborated with K. Wahl at the Naval Research Laboratory, we quantified the observed frequency shifts. By combining the QCM with a nanoindentor with a known contact force, we have established that the frequency shift of the QCM is proportional to the true area of contact, and have successfully modeled the results by extending an existing theory which treats the contact in the near-field acoustic regime.

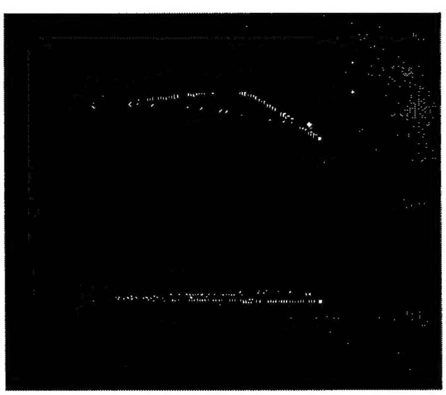


Our work has received considerable attention this year, most notably a writeup in the August 2003 edition of *Populuar Mechanics*. At the time of this report, we have completed the experiments originally proposed, and we continue to publish manuscripts based on the data collected in the funding period.

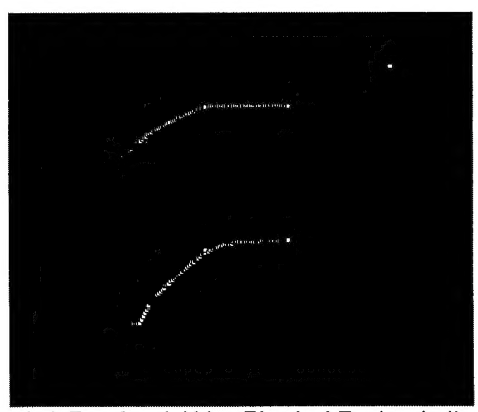
We have employed a quartz crystal microbalance technique, in conjunction with scanning tunneling microscopy, to study of the nanodynamical properties TCP reaction films formed at elevated temperatures in ultra-high vacuum conditions on high purity iron, chromium, iron oxide and chromium oxide surfaces. The data reveal trace levels of lateral interfacial slippage, potentially in conjunction with viscoelastic effects, for reaction films characterized by very low friction coefficients at the macroscale. In contrast, rigidly attached TCP reaction films are observed to form in systems characterized by high macroscopic friction coefficients. These results reveal a vital, and unexpected, link between atomic-scale lateral motion of a film and its macroscopic friction coefficient. Refs [1,5,6,8,11,13]



Frequency and quality factor shifts (or lac thereof) for systems that TCP does not lul at macroscopic length scales: Iron, chron and chromium oxide at 300 C and 400 C

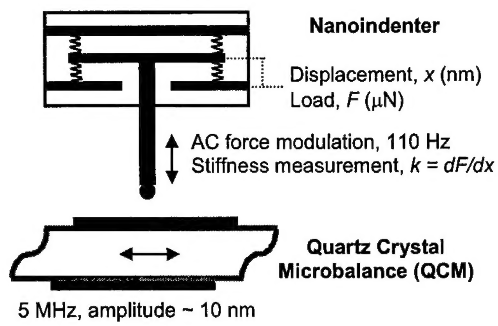


Frequency and quality factor shifts for systems that TCP does lubricate at macroscopic length scales: TCP/iron oxide and oyxgen/TCP/iron. The dissipation is consistent with trace levels of slippage, potentially in conjunction with viscoelasticity. No stress appears.



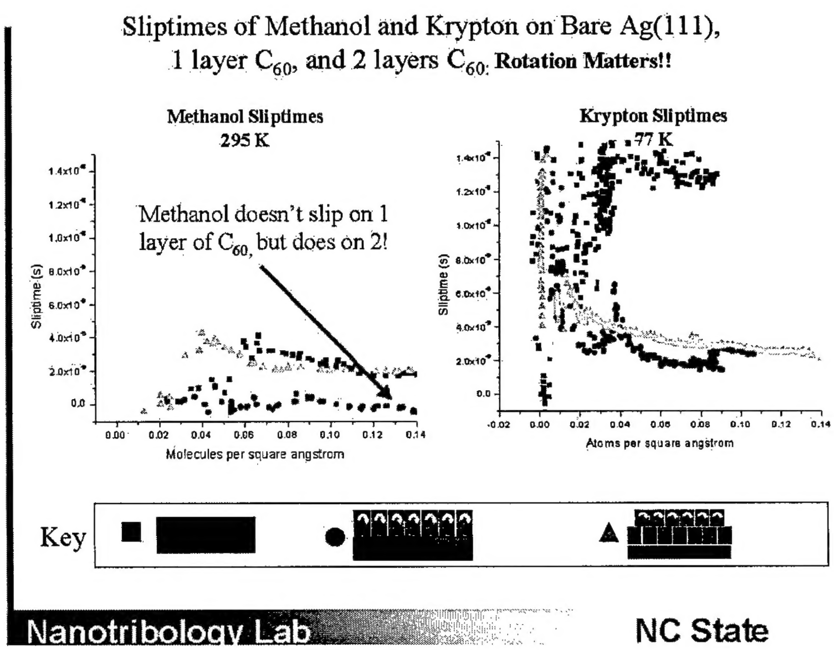
M. Abdelmaksoud, J. Bender, J. Krim, Physical Review Letters,

In order to study the lubricants' performance at realistic sliding speeds, we constructed an STM-QCM apparatus for imaging and friction experiments whereby the topography of the substrate is compared before, during and after tip-surface contact or tunneling contact though the lubricant layer. In collaboration with K. Wahl at the Naval Research Laboratory, we have quantified the observed frequency shifts. By combining the QCM with a nanoindentor with a known contact force, we have established that the frequency shift of the QCM is proportional to the true area of contact, and have successfully modeled the results by extending an existing theory which treats the contact in the near-field acoustic regime. The work is important to allow quantitative, rather than qualitative images to be obtained by means of the STM-QCM apparatus. Refs [1,3,7]



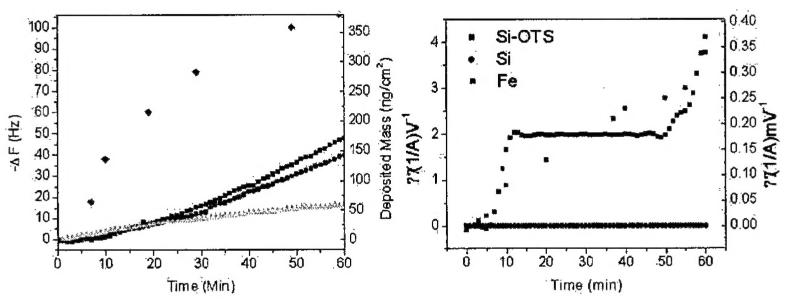
The Frequency shift of a QCM as a function of contact area (inferred from nanoindentation measurements), exhibits distinctly linear behavior.

Studies of interfacial slippage have also been performed with atomically thin hydrocarbon layers sliding on C60 monolayers and bilayers deposited on Ag (111) and Cu (111) substrates, to examine the impact of C60 molecular rotation on friction. C60 bilayers, with estimated rotational rates of 10^9 Hz exhibit lower friction than their non-spinning C60 monolayer counterparts. Refs [2,12,15]



We have also examined whether vapor phase lubricants are potentially compatible with OTS layers, the latter being a common surface treatment for MEMS systems. We observe that not only are the materials compatible, but in fact the combination exhibits nanotribological attributes that are desirable in macroscale lubricants. Refs. [4,7,9,10]

Promising results:TBBP adsorbs on OTS and the combination slips.



- Uptake of TBPP on Fe, Si and Si coated with OTS (octadecyltrichlorosilane)
- Change in frequency indicates mass uptake, change in amplitude indicates lateral slippage/molecular motion.

(3)Consultations/Technology Transitions

The work performed was carried out in close coordination with N. H. Forster at Wright-Patterson AFB, OH. Preliminary and final results were immediately conveyed to Forster, in order to speed the intermediate steps before introducing the technology into high speed rolling element bearings intended for use in gas turbine engines. The work was summarized at the annual AFOSR tribology workshops, where Krim was able to closely consult on the project with AFOSR-funded A. Gellman and Forster. The MEMS-related work is being performed in close collaboration with groups who fabricate micromechanical switches, and is coordinated with related efforts by M. Dugger at Sandia National Laboratories, and on AFOSR funded devices developed by P. Franzon at NCSU.

(4) Personnel Supported

Mohammed Abdelmaksoud (full time, Ph.D. and post-doctoral appointment); Tonya Coffey (graduate student, part time); Jonathan Bender (post-doctoral appointment, currently an assitant professor at the University of South Carolina); Jacqueline Krim (1 mo summer); David Adam Hook (undergraduate assistant); Cherno Jaye, full time graduate student.

(5) Invited talks at conferences including the results of AFOSR support: (11)
Euresco Conference on Electronic Structure, ``Out of the Vacuum", Touloun, France, September (2001); Acoustic Wave Workshop, Taos, NM August (2001) ; AFOSR/ONR/NSF Tribology Review, Duck Key, Fl, June (2001); American Association of Physics Teachers, Morehead City, NC, October (2001) ; American Chemical Society, Symposium on Friction, Orlando, FL., April (2002); European Physical Society, Brighton, Great Britain, April (2002); AFOSR Tribology&Quasicrystal Program Review, June (2002) ; International Workshop on Materials for Extreme Environments, Anchorage, Alaska, August (2002); European Science Foundation Workshop on Nanotribology, Portovenere, Italy, October, (2002); National Symposium of the American Vacuum Society, Denver, CO, Nov. (2002); Swiss-US Forum on Nanoscience and Nanotechnology: Nanomechanics and Single Molecule Research, Basel, Oct. (2003)

Invited seminars and colloquia including the results of AFOSR support: (23)
University of Tennesee, April 2001; Shaw University, Raleigh, NC, April 2001; Dartmouth College, Dartmouth, NH, May 2001; University of New Mexico, Albuquerque, August 2001 (for general audiences) ; University of New Mexico, Albuquerque, August 2001 (physics department colloquium); University of North Carolina Greensboro, October 2001 University of South Florida, Tampa, FL, October 2001; Rutgers University, Piscataway, NJ, February, 2002; Florida Atlantic University,February, 2002; Lehigh University, April 2002; Southern Oregon University, May 2002; University of Idaho, Moscow, July 2002; Fermilab, Illinois, August, 2002; Davidson College, September 2002; Illinois Wesleyan, Bloomington, IL, November 2002; University of Tennessee, November 2002; Kent State University, Ohio, January 2003; North Carolina AT&T, Greensboro, NC, February 2003; Hoffman La Roche, Inc. Nutley, NJ, March 2003; Eastern Michigan University, Ypsilanti, MI, April 2003; University of Dayton, Dayton, OH, April 2003; Yale University, New Haven, CT, May 2003; Duke University, Durham, NC, October 2003

Refereed Journal Articles

(1)"*Surface Science and The Atomic-Scale Origins of Friction: What Once was Old is New Again*", Millenium Volume of Surface Science on Frontiers in Surface and Interface Science, C.B. Duke and W. Plummer, eds.,Surf. Sci., **500** , 741-758 (2002)

(2)"*A Scanning Probe and Quartz Crystal Microbalance Study of the Impact of C60 on Friction at Solid-liquid Interfaces*", T.S. Coffey, M. Abdelmaksoud and J. Krim, J. Physics Cond. Matt., Special Issue, **13**, 4991-4999 (2001)

(3)"*Measuring Nanomechanical Properties of a Dynamic Contact Using an Indenter Probe and Quartz Crystal Microbalance,*" B. Borovsky, J. Krim, S.A.S. Asif and K.J. Wahl, J. Appl. Phys., **90,** 6391-6396 (2001)

(4)"*Study of Contacts in an Electrostatically Actuated Microswitch*", S. Majumder, N.E. McGruer, G.G. Adams, P.M. Zavracky, R.H. Morrison, J. Krim, Sensors and Actuators A-Physical, **93** (1) 19-26 Aug 25 2001

(5)"*Nanotribology of a Vapor-Phase Lubricant: A Quartz Crystal Microbalance Study of Tricresylphosphate (TCP) uptake on Iron and Chromium*," M. Abdelmaksoud, J. Bender and J. Krim, Tribology Letters, **13**, 179-186 (2002)

(6)"*Friction at Macroscopic and Microscopic Length Scales"*, J. Krim, American J. Phys., **70,** 890-897 (2002), invited Resource Letter

(7)"*Applications of the Piezoelectric Quartz Crystal Microbalance for Microdevice Development*", J.W. Bender and J. Krim, (invited) in Microdiagnostics, K. Breuer ed. (Springer Verlag, New York, 2004)

(8)"*Bridging the Gap between Macro- and Nanotribology: A Quartz Crystal Microbalance Study of Extreme Environment Lubrication*", M. Abdelmaksoud, J.Bender and J. Krim, Phys. Rev. Lett. **92,** 176101-1 - 176101-4 (2004)

(9)"*OTS Adsoption: A Dynamic QCM Study*", Y. Hussain, J. Krim and C. Grant, submitted to Jour. Coll. Inter. Sci.

(10)"*Nanodynamics of Vapor-Phase Organophosphates On Silicon and OTS for MEMS Lubrication Purposes*", W. Neeyakorn, M. Varma, C. Jaye, C. Grant and J. Krim, submitted to Tribology Letters

Proceedings Articles

(11)"*STM-QCM studies of Vapor Phase Lubricants*", B. Borovsky, M. Abdelmaksoud and J. Krim, in Nanotribology: Critical Assessment and Research Needs, S. Hsu and Z.C. Ying, eds. (Kluwer, Boston, 2002), pp. 361-375.

(12)"*A Scanning Probe and Quartz Crystal Microbalance Study of C60 on Mica and Silver (111) Surfaces*", T.S. Coffey, M. Abdelmaksoud and J. Krim, in *Fundamentals of Tribology and Bridging the Gap Between the Macro-and Micro/nanoscales*, B. Bhushan, ed., 171-176 (Kluwer, Dordrecht, 2001)

(13)"*Scanning Tunneling Microscope-Quartz Crystal Microweighing Studies of 'Real-World' and Model Lubricants*", J. Krim, M. Abdelmaksoud, B. Borovsky and S.M. Winder, in *Dynamics and Friction in Submicrometer Confining Systems*, Y. Braiman, J.M. Drake and F. Family, eds. (Oxford University Press, New York, 2004)

Other Articles

(14)"*Tribology*", J. Krim, Encyclopedia Italiana, G. Bedeschi, ed., in press, invited

(15)"*Quartz Crystal Microweighing*", T.S. Coffey and J. Krim, Encyclopedia of Nanoscience and Nanotechnology, H.S. Nalwa, ed, (American Scientific Publishers, Los Angeles, 2004) vol. 7, pp. 869-877, invited

(16) "*Foundations of Nanomechanics: From Solid-State Theory to Device Applications*", Book Review by J. Krim, Physics Today (May 2004) pp. 58-59.

Ph.D. dissertations:
Mohammed Abdelmaksoud, Ph.D., North Carolina State University (2001), "*Nanotribology of a Vapor Phase Lubricant: A Quartz Crystal Microbalance Study of Tricresylphosphate (TCP) Uptake on Iron and Chrome*" Present Position: Lecturer, Cairo University
Tonya Coffey, Ph.D., North Carolina State University (2004), "*Nanotribology Fundamentals: Predicting the Viscous Coefficient of Friction*" Present Position: Asst. Professor, Physics, Appalachian State University

(9) Honors/awards/other accomplishments:
Throughout the AFOSR award period, the PI's work has been widely recognized, as evidenced by the diverse nature of the invitations received for seminars, colloquia, conference presentations and review articles. The PI is on the editorial boards of Tribology Letters and Tribology Transactions, and the Advisory Editorial Board of Surface Science. She is a Fellow of the American Vacuum Society and the American Physical Society. She was selected as a Sigma XI Distinguished Lecturer for 2001-2003, the North Carolina State University Alumni Outstanding Researcher award (2002) and listed in Who's Who in Science on an ongoing basis.